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## PROCESS FOR THE PRODUCTION OF SILYL CARBOXYLATE MONOMERS

- 5 The present invention relates to the production of silyl carboxylate by a surprising new route.

Silyl carboxylates are useful as monomers or co-monomers in the production of metal-free binders for self polishing 10 antifouling paints as, for instance, disclosed in EP-A-1127902. Antifouling paints are widely used to improve the performance of ships by preventing the growth of marine organisms on the sub-marine parts of ship's hulls. Binders containing metals such as tin have been widely 15 used since the 1960's but research has shown that the organotin tributyl tin (TBT) causes environmental problems such as deformations in oysters and sex changes in whelks. Silyl carboxylates derived binders are an important replacement for such tin-based systems. Accordingly, the 20 economic production of silyl carboxylate monomers will make an important contribution to such systems.

Some of the polymers used in the above-described 25 antifouling paints are based on silylated carboxylate monomers.

Several processes are known as conventional techniques for the synthesis of said silylated carboxylate monomers.

- 30 EP 1260513 relates to a process for the preparation of trialkylsilylated carboxylate monomers from hexaalkyldisilylsulfates and metallic salts of unsaturated carboxylic acids.
- 35 US 6,498,264 discloses the reaction of chlorosilanes having bulky substituent groups with unsaturated acids to produce silyl esters.

JP 5306290 A describes a process to obtain a methacrylic functional group-containing organosilicon compound. The process comprises reacting methacrylic acid with a halogenoalkylsilane (e.g. trialkylsilylchloride) in the presence of a tertiary amine compound having a cyclic structure. This process has disadvantages such as the reduced availability and storage stability of the silyl chloride. Moreover, the reaction yields as a by-product a hydrogen halide (which provokes the corrosion of the production equipment) or a halide salt (which has to be removed by filtration).

The synthesis of trimethylsilyl methacrylate from methacrylic acid and hexamethyldisilazane is described in A.Chapman & A.D.Jenkins J.Polym.Sci. Polym.Chem.Edn. vol 15, p.3075 (1977).

JP 10195084 A discloses the reaction of unsaturated carboxylic acid such as acrylic acid or methacrylic acid with a trialkylsilylhydride compound in the presence of a copper catalyst. One of the disadvantages of this method is the risk of hydrogenation of the unsaturated carboxylic acid due to a side reaction of the produced H<sub>2</sub> on the carbon-carbon double bond.

Reaction mechanisms of nucleophilic attack at silicon have been disclosed in the literature. Bassindale et al, The Chemistry of Organic Silicon Compounds, chapter 13, J Wiley & Sons 1989, discloses extensive reaction mechanisms for silicon. However, the nucleophilic reaction mechanisms relate to halo substituted silicon type compounds and these are encouraged by the halogen leaving group.

EP 056108A1 (Dow Corning Corporation) discloses the acid catalysed reaction of alkoxy silanes with carboxylic acids to produce alkyl carboxylates and disiloxanes.

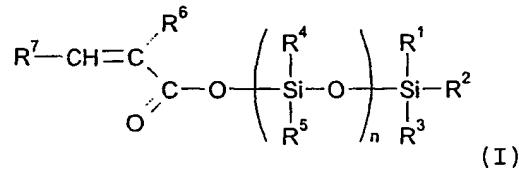
- 5 Nakao et al, Bulletin of the Chemical Society Japan, 54, 1267-1268 (1981) discloses the esterification of carboxylic acids with alcohols in the presence of trimethyl chlorosilane. The reaction is said to proceed via the intermediate alkoxy trimethyl silane and produces  
10 10 the alkyl ester in high yield together with disiloxane. The yields of methyl acetate are 96-98%.

15 It is one of the objects of the present invention to provide a process for the production of silyl carboxylates.

20 It is a further object of the present invention to provide a more convenient and efficient process for the production of silyl carboxylates.

According to a first aspect of the present invention there is provided a process for the production of hydrocarbyl silyl unsaturated carboxylates of formula (I).

25



wherein

- 30  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  each independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxy, aryl, aryloxy, aralkyloxy,  $-\text{O}-\text{SiR}^1\text{R}^2\text{R}^3$ ,  $-\text{O}-\text{(SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$  or aralkyl radical optionally substituted by one or more substituents independently selected from the group

comprising alkyl, alkoxy, aralkyl, aralkyloxy, aryl, aryloxy, silyl, -O-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>, -O-(SiR<sup>4</sup>R<sup>5</sup>O)<sub>n</sub>-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>, hydroxyl, halogen, amino or amino alkyl radicals, or may independently be an -O-C(O)-C(R<sup>6</sup>)=CHR<sup>7</sup> group;

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R<sup>6</sup> represents a hydrogen atom, or an alkyl group, or (-R<sup>11</sup>-)C(O)OR<sup>10</sup> wherein R<sup>10</sup> represents an hydrogen atom, -(SiR<sup>4</sup>R<sup>5</sup>O)<sub>n</sub>-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> are as already defined or an alkyl group; wherein R<sup>11</sup> is independently

10 selected from alkyl, alkenyl, alkynyl, aryl or an aralkyl radical optionally substituted by one or more substituents independently selected from alkyl, alkenyl, alkynyl, aralkyl, aryl, hydroxyl, halogen, amino or amino alkyl radicals; O=O or 1;

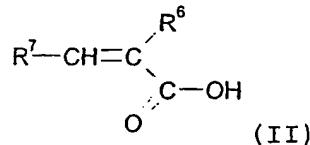
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R<sup>7</sup> represents a hydrogen atom, or independently represents alkyl, aryl, aralkyl, alkenyl, alkynyl radical optionally substituted with the same radicals as defined for R<sup>6</sup> above or R<sup>7</sup> represents -COOR<sup>9</sup> wherein R<sup>9</sup> represents an hydrogen atom, an alkyl group or -(SiR<sup>4</sup>R<sup>5</sup>-O)<sub>n</sub>-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> wherein R<sup>1</sup>,

20 R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are as already defined;

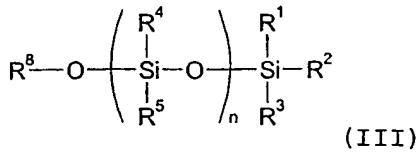
by reaction of an unsaturated carboxylic acid of formula (II)

25



wherein R<sup>6</sup> and R<sup>7</sup> in formula (II) are as defined above; with a hydrocarbyl silyl compound of formula (III)

30



wherein  $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$  and  $\text{R}^5$  are as defined above and  $\text{R}^8$  is an hydrogen atom, an alkyl, aralkyl or aryl, alkenyl or alkynyl group optionally substituted with one or more substituents selected from the equivalent substituents as detailed for  $\text{R}^1-\text{R}^5$  above; and each  $n$  above independently represents a number of dihydrocarbylsiloxane units from 0 to 1000; the said reaction being carried out in the presence of a silaphilic catalyst.

Preferably, wherein when  $\text{R}^{10}$  represents alkyl or hydrogen in formula II, it represents  $-(\text{SiR}^4\text{R}^5\text{O})_n\text{SiR}^1\text{R}^2\text{R}^3$  in formula I, wherein  $n$  and  $\text{R}^1-\text{R}^5$  are as defined previously.

Preferably, wherein when  $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$  or  $\text{R}^5$  are aryloxyl, alkaryloxyl, alkoxy or hydroxyl in formula III, they may represent  $-\text{O}-\text{C}(\text{O})-\text{C}(\text{R}^6)=\text{CHR}^7$  in formula I.

Preferably, where  $\text{R}^9$  represents an alkyl group or an hydrogen atom in formula (II), it may represent  $-(\text{SiR}^4\text{R}^5\text{O})_n\text{SiR}^1\text{R}^2\text{R}^3$  in formula (I).

Preferably, the silaphilic catalysts are selected from fluoride containing mineral or organic salts which comprise, but are not limited to, sodium fluoride, potassium fluoride, caesium fluoride or tetrabutyl ammonium fluoride ( $\text{Bu}_4\text{NF}$ ); or are selected from N-methyl imidazole (NMI), N,N-dimethylamino pyridine (DMAP), hexamethylphosphoric triamide (HMPA), 4,4 dimethyl imidazole, N-methyl-2-pyridone (NMP), pyridine N-oxide, triphenylphosphine oxide, 2,4 dimethyl pyridine, N-methyl-4-pyridone, dimethyl formamide (DMF), 3,5 dimethyl pyridine, N,N-dimethylethylene Urea (DMEU), N,N-

dimethylpropylene Urea(DMPU), pyridine, imidazole, trimethylamine, dimethyl sulphoxide(DMSO), N-methyl pyrrolidinone(NMP), formamide, N-alkylformamides, N,N-dialkylformamides, acetamide, N-alkylacetamides, N,N-dialkylacetamides, alkylcyanides, N-methyl pyrrolidone, p-dimethylaminobenzaldehyde, 1,2-dimethyl imidazole, LiOH, LiStearate, NaI, MeONa or MeOLi; the term alkyl in the above N-alkyl and N,N-dialkyl . . . . amides and cyanides include any linear, cyclic, bicyclic, polycyclic, alkyl 10 aliphatic or aromatic group and in the case of N,N-compounds the alkyl may be the same or different, an example is N-formyl Rosinamine.

Silaphilic catalysts have been defined as molecules having 15 a special affinity for silicon - Brook, Silicon in Organic, Organometallic and Polymer Chemistry section 5.5, J Wiley & Sons 2000. Preferably, the silaphilic catalysts have an electron rich heteroatom such as oxygen or nitrogen. Typically, the hetero atom is substituted with 20 electron donating groups.

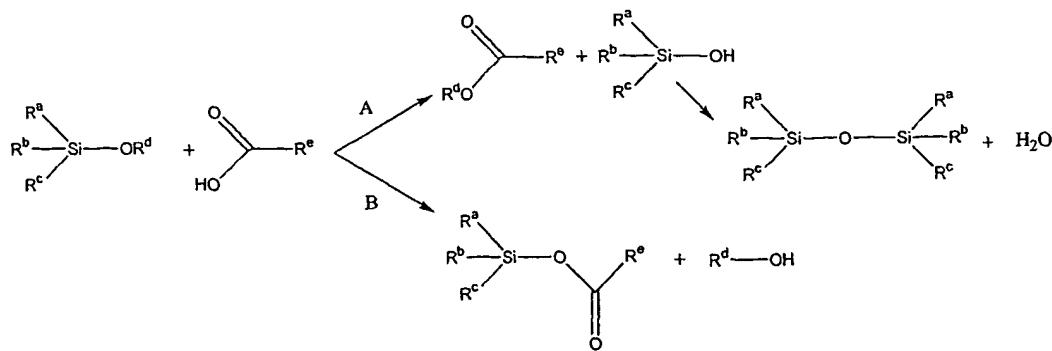
Lewis acid catalysts may also be used to catalyse the process of the present invention. Accordingly, for the purposes of the present invention, the term "silaphilic 25 catalyst" should be taken as incorporating Lewis acid catalysts such as titanium butoxide  $Ti(OBu)_4$ .

Said catalyst may, for example, be a metal alkoxide, an organic tin compound such as dibutyltin dilaurate, 30 dibutyltin dioctate or dibutyltin diacetate, or a boron compound such as boron butoxide or boric acid. Illustrative examples of metal alkoxide include aluminum triethoxide, aluminum triisopropoxide, aluminum tributoxide, aluminum tri-sec-butoxide, aluminum 35 diisopropoxy-sec-butoxide, aluminum diisopropoxyacetyl acetonate, aluminum di-sec-butoxyacetyl acetanoate, aluminum diisopropoxyethyl acetoacetate, aluminum di-sec-

butoxyethylacetacetate, aluminum trisacetyl acetonate, aluminum triethylacetacetate, aluminum acetylacetone, bisethylacetacetate, titanium tetraethoxide, titanium tetraisopropoxide, titanium (IV) butoxide, titanium 5 diisopropoxybisacetyl acetonate, titanium diisopropoxybisethyl acetoacetate, titanium tetra-2-ethylhexyloxide, titanium diisopropoxybis(2-ethyl-1,3-hexanediolate), titanium dibutoxybis(triethanolamine), zirconium tetrabutoxide, zirconium tetraisopropoxide, 10 zirconium tetramethoxide, zirconium tributoxide monoacetylacetone, zirconium dibutoxide bisacetylacetone, zirconium butoxide trisacetylacetone, zirconium tetraacetylacetone, zirconium tributoxide monoethylacetacetate, zirconium dibutoxide 15 bisethylacetacetate, zirconium butoxide triethylacetacetate and zirconium tetraethylacetacetate. In addition to these compounds, cyclic 1,3,5-triisopropoxycyclotritrialuminioxane and the like can also be used and is thereby incorporated within the 20 definition of "silaphilic catalyst".

Preferably, in compounds of formula I, the number of (alk)acryloyl groups is less than 4, more preferably, less than 3, most preferably 1.

25 Advantageously, although the prior art describes the reaction of alkoxy silanes with carboxylic acid as leading to the corresponding alkylcarboxylates and the silanol (path A), the latter tending to dehydrate to form 30 disiloxanes. It has been surprisingly discovered that the use of a silaphilic catalyst (ie. a catalyst able to coordinate in a reversible manner with the silicon atom) allows preferential substitution of alkoxy or hydroxyl groups by the carboxy group (path B).



Advantageously, the process of the present invention  
5 results in the release of harmless by-products, namely  
water and methanol.

More preferably, the silaphilic catalyst is a catalyst  
capable of facilitating a penta or hexa coordinated  
10 silicon species in the transition state of the reaction.

More, preferably, the silaphilic catalysts are  
independably selected from

15 DMF, DMSO, formamide, N-alkylformamides, N,N-  
dialkylformamides, acetamide, N-alkylacetamides, N,N-  
dialkylacetamides, N-Methyl pyrrolidone, p-  
dimethylaminobenzaldehyde, DMAP, N-methyl imidazole, 1,2-  
dimethyl imidazole, HMPA, DMPU, NaI, MeONa, MeOLi, Bu4NF,  
20 Ph3PO, LiOH, Listearate and pyridine N-oxide.

The catalysts may be homogenous or heterogenous but  
preferably, are homogenous and present in a free form in  
the reaction medium. Alternatively, the catalysts may be  
25 bonded to a polymeric support.

Particularly preferred catalysts are independably selected  
from

DMF, formamide, N-alkyl formamide, N,N-dialkylformamide, Bu<sub>4</sub>NF.

5 Preferably, the catalysts are present at a level of 0.001-100 mol% (mol/mol silane), more preferably 0.01-40 mol%, most preferably, 0.1-30 mol% in the reaction medium at the start of the reaction. Especially preferred is a range of 20-30 mol% for the formamides or 0.1-1mol% for Bu<sub>4</sub>NF.

10

Preferably, the reaction includes a polymeric inhibitor. A suitable polymerisation inhibitor is o-methoxyphenol.

15

Preferably, the reaction is carried out in a suitable solvent.

Suitable solvents which can be used in the process of the invention include non polar inert solvents, aliphatic hydrocarbons, cyclic and non cyclic ethers.

20

Suitable solvents may be independently selected from pentane, hexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthlene, diethyl ether, diisopropyl ether, diisobutyl ether or mixtures thereof.

30

Especially preferred solvents are those which allow reactive distillation ie. which cause no distillation of any of the reactants but which allow preferential distillation of one of the products to drive the equilibrium to the right.

35

More especially preferred solvents are those which form a low boiling azeotrope with the distilled R<sup>8</sup>OH. Still more especially preferred solvents are those which form a heterogenous low boiling azeotrope with the distilled R<sup>8</sup>OH.

Most preferably, the solvents are independently selected from pentane, hexane, heptane, toluene and xylene.

Preferably, the temperature of the reaction depends on the  
5 boiling point of the azeotrope that has to be distilled,  
the shape of the reactor and the height of the  
distillation column.

Typically, the reaction is carried out in the range 0°C -  
10 200°C, more preferably, 60-170°C, most preferably, 110-  
140°C.

Preferably, the polymerisation inhibitor is present in the  
range 0.001-10% wt/wt of the total reaction mix, more  
15 preferably 0.001-5% wt/wt and most preferably 0.01-2%  
wt/wt.

Preferably, the molar ratio of silane:acid is between  
1:100 and 50:1, more preferably between 10:1 and 1:10,  
20 most preferably, between 2:1 and 1:2. Preferably, the  
molar ratio of silane:acid is approximately 1:1.

Preferably, the solvent is at least 10 wt% of the total  
reaction mix at the start of the reaction, more  
25 preferably, at least 20 wt%, most preferably, at least 30  
wt%. The reaction may be carried out at atmospheric  
pressure although both higher and lower pressures are also  
possible.

30 The reaction may also be performed without solvent and  
accordingly suitable ranges of solvent are 0-99 wt% of the  
total reaction mix, more preferably, 20-50 wt%, most  
preferably 30-40 wt%.

35 Preferably, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> each independently  
represent hydrogen, alkyl, alkynyl, aryl or aralkyl  
radicals optionally substituted as aforesaid in the first

aspect of the present invention, more preferably, optionally substituted by one or more substituents independently selected from the group comprising alkyl, aralkyl, aryl, silyl, halogen, tertiary amino or amino 5 alkyl radicals.

Preferably, R<sup>6</sup> represents an hydrogen atom or an alkyl group.

10 Preferably, R<sup>7</sup> represents an alkyl group, an aryl group or an aralkyl group.

Preferably, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> each independently represent an alkyl, an aryl group or a hydrogen atom.

15 According to an embodiment of the present invention, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>9</sup> are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl.

20 Preferably, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>9</sup> are methyl and R<sup>7</sup> is hydrogen.

Preferably, R<sup>8</sup> represents a hydrogen atom or an alkyl group.

25 When R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are alkyl groups they are preferably, independently selected from the group consisting of C1 to C8 alkyl groups, preferably C3 and C4, more preferably isopropyl and n-butyl. The said alkyl groups may be branched or linear and, optionally, they may be 30 substituted as aforesaid in the first aspect.

Preferably, when any one of R<sup>1</sup>-R<sup>5</sup> is selected as -O-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> or -O-(SiR<sup>4</sup>R<sup>5</sup>O)<sub>n</sub>-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> the R<sup>1</sup>-R<sup>5</sup> groups attached to the silicon radical in the selected group are not themselves, 35 -O-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> or -O-(SiR<sup>4</sup>R<sup>5</sup>O)<sub>n</sub>-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>. Preferably, when any one of the R<sup>1</sup>-R<sup>5</sup> groups is selected as -O-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> or -O-(SiR<sup>4</sup>R<sup>5</sup>O)<sub>n</sub>-SiR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> and such groups are substituted, the

substitution is at the R<sup>1</sup>-R<sup>5</sup> groups and is preferably, by alkyl, alkoxy, aralkyl, aralkyloxy, hydroxyl, aryl, aryloxy, silyl, halogen, amino or amino alkyl, more preferably, alkyl or aryl, most preferably, alkyl.

5

Preferably, each n in formulas I, II or III is independently 0 to 50, more preferably, 0 to 10, most preferably 0 to 5. Especially preferred values for n are selected from 0, 1, 2, 3, 4 or 5.

10

As used herein, the term "polymer" refers to the product of a polymerisation reaction, and is inclusive of homopolymers, copolymers, terpolymers, etc.

15 As used herein, the term "copolymer" refers to polymers formed by the polymerisation reaction of at least two different monomers.

As used herein, the term "independently selected" or  
20 "independently represent" indicates that the each radical R so described, can be identical or different. For example each R<sup>4</sup> in compound of formula (I) may be different for each value of n.

25 The term "alkyl", as used herein unless otherwise defined, relates to saturated hydrocarbon radicals having straight, branched, cyclic or polycyclic moieties or combinations thereof and contains 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms,  
30 still more preferably 1 to 6 carbon atoms, yet more preferably 1 to 4 carbon atoms. Examples of such radicals include may be independently selected from methyl, ethyl, n-propyl, isopropyl n-butyl, isobutyl, set-butyl, tert-butyl, 2-methylbutyl, pentyl, iso-amyl, hexyl, cyclohexyl,  
35 3-methylpentyl, octyl and the like.

The term "alkenyl", as used herein, relates to hydrocarbon radicals having one or several double bonds, having straight, branched, cyclic or polycyclic moieties or combinations thereof and containing from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of alkenyl groups include vinyl, allyl, isopropenyl, pentenyl, hexenyl, heptenyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, 1-propenyl, 2-but enyl, 2-methyl-2-butenyl, isoprenyl, farnesyl, geranyl, geranylgeranyl and the like.

The term "alkynyl", as used herein, relates to hydrocarbon radicals having one or several triple bonds, having straight, branched, cyclic or polycyclic moieties or combinations thereof and having from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably from 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of alkynyl radicals include ethynyl, propynyl, (propargyl), butynyl, pentynyl, hexynyl and the like.

The term "aryl" as used herein, relates to an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, and includes any monocyclic, bicyclic or polycyclic carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. Said radical may be optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aryl includes phenyl, p-tolyl, 4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl,

3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and  
5 the like.

The term "aralkyl" as used herein, relates to a group of the formula alkyl-aryl, in which alkyl and aryl have the same meaning as defined above. Examples of aralkyl  
10 radicals include benzyl, phenethyl, dibenzylmethyl, methylphenylmethyl, 3-(2-naphthyl)-butyl, and the like.

The term "silyl" as used herein includes  $-SiR^1R^2R^3$  and  $-(SiR^4R^5O)_n-SiR^1R^2R^3$  groups wherein  $R^1-R^5$  are as defined  
15 herein. Preferably when the  $R^1, R^2, R^3, R^4$  or  $R^5$  group in formula (I) is substituted by such a silyl group at least one or more of  $R^1, R^2, R^3, R^4$  and  $R^5$  in the silyl group  $-SiR^1R^2R^3$  or  $-(SiR^4R^5O)_n-SiR^1R^2R^3$  are alkyl or aryl and at least one or more of  $R^1, R^2, R^3, R^4$  and  $R^5$  in the said silyl  
20 group which are not alkyl or aryl are  $-O-SiR^1R^2R^3$  or  $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$ .

In the silyl  $-SiR^1R^2R^3$  or  $-(SiR^4R^5O)_n-SiR^1R^2R^3$ , if  $R^1$  is alkyl or aryl and at least one of  $R^2$  and  $R^3$  is  $-O-SiR^1R^2R^3$   
25 or  $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$  then, preferably,  $R^1, R^2, R^3, R^4$  and  $R^5$  in such  $-O-SiR^1R^2R^3$  or  $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$  groups are themselves alkyl or aryl and may be the same or different, more preferably, each independently may be C<sub>1</sub> - C<sub>8</sub> alkyl groups.

30 Examples of the ethylenically unsaturated part of formula (I) may include but are not limited to (meth)acrylate, itaconate, methyl fumarate, methyl maleate, n-butyl fumarate, n-butyl maleate, amyl fumarate, amyl maleate,  
35 and the like and polymers or copolymers thereof, wherein methacrylate or acrylate is herein collectively referred to as a "(meth)acrylate".

In a preferred embodiment, said ethylenically unsaturated part of formula (I) is (meth)acrylate, and copolymers or polymers thereof.

5

Examples of the organosilylated carboxylate monomers of general formula (I) include but are not limited to tri-n-butyl 1-(meth)acryloyloxy-silane, tri-n-propyl-1-(meth)acryloyloxy silane, tri-t-butyl-1-(meth)acryloyloxy-

10 silane, tri-isopropyl-1-(meth)acryloyloxy-silane, tri-isobutyl-1-(meth)acryloyloxy-silane, tri-methyl-1-

(meth)acryloyloxy-silane, triethyl- 1-(meth)acryloyloxy-silane, tribenzyl- 1-(meth)acryloyloxy-silane, triamyl- 1-

15 (meth)acryloyloxy-silane, triphenyl- 1-(meth)acryloyloxy-silane, nonamethyl-1-(meth)acryloyloxy-tetrasiloxane,

nonaethyl-1-(meth)acryloyloxy-tetrasiloxane, nona-t-butyl-1-(meth)acryloyloxy-tetrasiloxane, nonabenzyl-1-

(meth)acryloyloxy-tetrasiloxane, nona-isopropyl-1-(meth)acryloyloxy-tetrasiloxane,

20 nona-n-propyl-1-(meth)acryloyloxy-tetrasiloxane, nona-isobutyl-1-(meth)acryloyloxy-tetrasiloxane,

(meth)acryloyloxy-tetrasiloxane, nona-amyl-1-(meth)acryloyloxy-tetrasiloxane,

25 (meth)acryloyloxy-tetrasiloxane, nona-n-butyl-1-(meth)acryloyloxy-tetrasiloxane, nona-dodecyl-1-

(meth)acryloyloxy-tetrasiloxane, nona-hexyl-1-(meth)acryloyloxy-tetrasiloxane,

30 (meth)acryloyloxy-tetrasiloxane, nona-phenyl-1-(meth)acryloyloxy-tetrasiloxane, nona-octyl-1-

(meth)acryloyloxy-pentasiloxane, undecamethyl-1-(meth)acryloyloxy-pentasiloxane,

35 (meth)acryloyloxy-pentasiloxane, undecaethyl-1-(meth)acryloyloxy-pentasiloxane, undeca-t-butyl-1-

(meth)acryloyloxy-pentasiloxane, undecabenzyl-1-(meth)acryloyloxy-pentasiloxane,

undeca-isopropyl-1-(meth)acryloyloxy-pentasiloxane, undeca-n-propyl-1-(meth)acryloyloxy-pentasiloxane,

undeca-isobutyl-1-(meth)acryloyloxy-pentasiloxane, undeca-amyl-1-(meth)acryloyloxy-pentasiloxane,

undeca-n-butyl-1-(meth)acryloyloxy-pentasiloxane, undeca-dodecyl-1-(meth)acryloyloxy-pentasiloxane,

undeca-hexyl-1-(meth)acryloyloxy-pentasiloxane,

(meth)acryloyloxy-pentasiloxane, undeca-phenyl-1-  
(meth)acryloyloxy-pentasiloxane, undeca-octyl-1-  
(meth)acryloyloxy-pentasiloxane tridecamethyl-1-  
(meth)acryloyloxy-hexasiloxane, tridecaethyl-1-  
5 (meth)acryloyloxy-hexasiloxane, trideca-t-butyl-1-  
(meth)acryloyloxy-hexasiloxane, tridecabenzyl-1-  
(meth)acryloyloxy-hexasiloxane, trideca-isopropyl-1-  
(meth)acryloyloxy-hexasiloxane, trideca-n-propyl-1-  
(meth)acryloyloxy-hexasiloxane, trideca-isobutyl-1-  
10 (meth)acryloyloxy-hexasiloxane, trideca-amyl-1-  
(meth)acryloyloxy-hexasiloxane, trideca-n-butyl-1-  
(meth)acryloyloxy-hexasiloxane, trideca-dodecyl-1-  
(meth)acryloyloxy-hexasiloxane, trideca-hexyl-1-  
(meth)acryloyloxy-hexasiloxane, trideca-phenyl-1-  
15 (meth)acryloyloxy-hexasiloxane, trideca-octyl-1-  
(meth)acryloyloxy-hexasiloxane 1,3,3,3-tetramethyl-1-  
trimethylsilyloxy-1-(meth)acryloyloxy-disiloxane,  
1-ethyl,3,3,3-trimethyl-1-trimethylsilyloxy-1-  
(meth)acryloyloxy-disiloxane,  
20 tris-(trimethylsilyloxy)-1-methacryloyloxy-silane and  
polymers thereof.

In formula I, the ethylenic unsaturated part is most  
preferably selected from acrylate and methacrylate.

25

The invention will now be described by way of illustration  
only and with reference to the accompanying examples.

In the following examples, NMR data has been determined in  
30 CDCl<sub>3</sub>, and are expressed as delta versus TMS.

Example 1:

A mixture of 20 g of methoxytributyl silane (CAS RN:15811-  
64-0), 8.12 g of methacrylic acid, 1.89 g of N,N-  
35 dimethylformamide, 0.2 g of p-methoxyphenol and 30 ml of  
heptane is heated until methanol is completely distilled

at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl methacrylate (89%).

5 Tri-n-butylsilyl methacrylate:  $^{13}\text{C}$  NMR : 167.8, 137.9,  
126.0, 26.7, 25.5, 18.5, 13.5, 14.0;  $^{29}\text{Si}$  NMR : 23.1; IR  
(film): 2959, 2927, 1703, 1334, 1174, 886, 766  $\text{cm}^{-1}$ .

Example 2:

10 A mixture of 10 g of tributyl silanol (CAS RN: 18388-85-  
7), 4.26 g of methacrylic acid, 0.94 g of N,N-dimethylformamide, 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until water is completely distilled at atmospheric pressure (b.p. of the azeotrope: 79.2°C) to furnish tributylsilyl methacrylate.

15

Comparative Example:

20 A mixture of 10 g of methoxytributyl silane, 4.26 g of methacrylic acid, 1.3 g of Amberlyst A15 (sulfonic acid resin), 0.1 g of p-methoxyphenol and 10 ml of heptane is heated. After distillation of heptane, only slight amounts of tributylsilyl methacrylate are detected, hexabutyl disiloxane and methyl methacrylate are present as main products.

25 Example 3:

30 A mixture of 10 g of tributyl silanol, 4.26 g of methacrylic acid, 0.58 g of formamide, 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until water is completely distilled at atmospheric pressure (b.p. of the azeotrope: 79.2°C) to furnish tributylsilyl methacrylate.

Example 4:

35 A mixture of 10 g of methoxytributyl silane, 4.26 g of methacrylic acid, 1.13 g of N,N-dimethyl acetamide, 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until

methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl methacrylate.

5   Example 5:

A mixture of 10 g of methoxytributyl silane, 4.26 g of methacrylic acid, 2.0 g of N-formyl Rosinamine (prepared as described in example 1 of WO00/55117), 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until  
10   methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl methacrylate.

Example 6

15   0.274 g of tetrabutylammonium fluoride trihydrate and 30 ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 20 g of methoxytributyl silane, 8.12 g of methacrylic acid and 0.2 g of p-methoxyphenol were then added. The mixture was heated  
20   until methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) for 2 h. Evaporation of the solvent under reduced pressure followed by vacuum distillation furnished pure tributylsilyl methacrylate.

25

Example 7

0.179 g of tetrabutylammonium fluoride trihydrate and 20ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 10 g of triisopropylsilanol,  
30   4.41 g of acrylic acid and 0.2 g of p-methoxyphenol were then added. The mixture was heated until the water is totally distilled at atmospheric pressure (b.p. of the azeotrope: 79.2°C) to furnish triisopropyl acrylate.

Triisopropylsilyl acrylate:  $^{13}\text{C}$  NMR: 132.5, 130.4, 175.0,  
35   12.3, 17.0;  $^{29}\text{Si}$  NMR: 21.84; IR (film): 2948, 2870, 1708, 1620, 1465, 1403, 1290, 1209, 1046, 884, 818,  $\text{cm}^{-1}$ .

Example 8

0.132 g of tetrabutylammonium fluoride trihydrate and 20ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 13.8 g of nonamethyl-1-

5 methoxy-tetrasiloxane (CAS: 78824-97-2), 4.41 g of methacrylic acid and 0.1 g of p-methoxyphenol were then added. The mixture was heated until the methanol is totally distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish nonamethyl-1-  
10 methacryloyloxy-tetrasiloxane.

Nonamethyl-1-methacryloyloxy-tetrasiloxane:  $^{13}\text{C}$  NMR: 166.8, 126.3, 137.8, 18.1, 1.95, 1.24, 1.03, -0.13;  $^{29}\text{Si}$  NMR: 7.3, -8.8, -20.1, -21.6; IR (film): 2963, 1730, 1372, 1260, 1083, 1045, 841, 809  $\text{cm}^{-1}$ .

15

Comparative example 2 shows the behaviour of an uncatalysed reaction, the reaction is very slow and leads to a mixture of starting materials and MMA.

20 Comparative example 2

A mixture of 20 g of methoxytributyl silane, 8.12 g of methacrylic acid, 0.2 g of p-methoxyphenol and 30 ml of heptane is heated. After 7 h at 165 °C only 0.15 eq. of methanol was distilled. Analysis of the reaction mixture  
25 by GC showed a mixture of starting materials, TBSiMA and methyl methacrylate.

Example 9:

30 0.36 g of lithium hydroxide monohydrate and 20ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 20 g of methoxytributylsilane, 8.12 g of methacrylic acid and 0.2 g of p-methoxyphenol were then added. The mixture was heated until the methanol is totally distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl  
35 methacrylate (88%).

Example 10:

A mixture of 21.9 g of 1,1,1,3,5,5-heptamethyl-3-methoxytrisiloxane (CAS RN:7671-19-4), 8.12 g of 5 methacrylic acid, 1.89 g of N,N-dimethylformamide, 0.2 g of p-methoxyphenol and 30 ml of heptane is heated until methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish 1,3,3,3-tetramethyl-1-trimethylsilyloxy-1-(meth)acryloyloxy-disiloxane.

1,3,3,3-tetramethyl-1-trimethylsilyloxy-1-(meth)acryloyloxy-disiloxane:  $^{13}\text{C}$  NMR : 166.4, 137.7, 126.30, 18.5, 1.7, -2.7;  $^{29}\text{Si}$  NMR : 10.1, -57.8; IR (film): 2962, 1708, 1453, 1336, 1312, 1256, 1184, 1090, 15 1009, 953, 846, 800, 758  $\text{cm}^{-1}$ .

The reaction temperatures for the above mentioned examples are as follows:-

20	Example #	T°
	1	150-170°C
	2	120-130°C
	3	120-140°C
	4	130-150°C
25	5	125-130°C
	6	110-120°C
	7	125-130°C
	8	110-135°C
	9	125-150°C
30	10	150-170°C

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to 35 this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, 5 except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be 10 replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

15

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any 20 accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.